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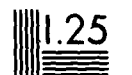UNCLASSIFIED   TR-9   NL

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Two good syntheses of the rare tube silicate litidionite, $NaKCuSi_4O_{10}$, are reported. In one a 2:1:1:8 mole-ratio mixture of CuO, Na_2CO_3, K_2CO_3, and SiO_2 is sintered and in the other a glass made from a mixture of these reagents in the same mole ratios is devitrified. The structures of the ion in this silicate and those in other known tube silicates are discussed in terms of their relationships to each other and to the ions in other silicates. It is pointed out that many latticework tubes like those which are the parents of—

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Synthesis of the Tube Silicate Litidionite and Structural

Relationships between It and Some Other Silicates

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Abstract

Two good syntheses of the rare tube silicate litidionite, $NaKCuSi_4O_{10}$, are reported. In one a 2:1:1:8 mole-ratio mixture of CuO, Na_2CO_3, K_2CO_3, and SiO_2 is sintered and in the other a glass made from a mixture of these reagents in the same mole ratios is devitrified. The structures of the ion in this silicate and those in other known tube silicates are discussed in terms of their relationships to each other and to the ions in other silicates. It is pointed out that many latticework tubes like those which are the parents of these tube silicate ions exist and it is concluded that silicate ions corresponding to some of them will be found.

While the scroll silicate chrysotile, $Mg_3Si_2O_5(OH)_4$[4,5] is a familiar item of commerce (it is one of the silicates commonly called asbestos) and has been extensively studied,[6] tube silicates and aluminosilicates are unfamiliar and have been investigated relatively little. They are interesting, however, because tube structures in which the tube bonds are primary bonds have received little attention.

The most studied of the tube silicates and aluminosilicates is the aluminosilicate imogolite, $Al_2(OH)_3SiO_3OH$.[7] It is known to be composed of neutral tubes (the details of the structure of these tubes are, however, not understood).[8] Another aluminosilicate which can be viewed as belonging to the tube group, since it has an aluminosilicate ion that can be considered to be tubular, is bavenite, $Ca_4Be_2Al_2Si_9O_{26}(OH)_2$.[9-11]

Three silicates which have tube ions are litidionite, $NaKCuSi_4O_{10}$,[13] fenaksite, $NaKFeSi_4O_{10}$,[14] and the synthetic species, $Na_2CuSi_4O_{10}$.[15] Others are agrellite, $NaCa_2Si_4O_{10}F$,[16] narsarsukite, $Na_2TiSi_4O_{11}$,[17] miserite, $KCa_5Si_2O_7Si_6O_{15}(OH)F$,[18] and probably canasite, $Na_4K_2Ca_5Si_{12}O_{30}(OH,F)_4$.[19]

As implied all but $Na_2CuSi_4O_{10}$ have been found naturally.[20-25] So far as is known fenaksite, agrellite, narsarsukite, miserite, and canasite are rare. Litidionite is apparently very rare, the only reported occurrence of it being in the crater of Mt. Vesuvius.

Both litidionite[15,26] and narsarsukite[27] have been made in the laboratory using hydrothermal techniques. Hydrothermal techniques have also been used to make $Na_2CuSi_4O_{10}$.[28-31]

Since compounds containing tube ions are uncommon, these silicates are of interest and good synthetic routes to them are of value. In this paper we report two good new syntheses for litidionite and point out the advantages of each.

In addition we discuss the structure of its silicate ion, Figure 1, and those of other known tube silicates in terms of their relationships to each other and to the ions in other silicates. We also point out the fact that many latticework tubes like those which are the parents of these tube silicate ions exist and conclude that silicate ions corresponding to some of them will be found.

Experimental

Synthesis of $NaKCuSi_4O_{10}$. Sintering Method. A mixture of $CuO(3.82g)$, $Na_2CO_3(2.54g)$, $K_2CO_3(3.32g)$, and $SiO_2(11.5g)$ (a 2:1:1:8 mole-ratio mixture) in a platinum crucible was heated in a muffle furnace to 725°C over ∿1h, held at this temperature for 1d, heated to 765°C over ∿1h, and held at this temperature for 6d. The product, a hard, porous, blue solid with black impurities dispersed throughout it (18.8g) was carefully broken out of the crucible (17.3g).

This material was crushed with a diamond mortar to a powder which was almost all <100 mesh. The very small fraction of it which was >100 mesh was rejected. A mixture of some (3.0g) of the remaining powder and distilled water buffered to a pH of 5 with potassium acid phthalate and sodium hydroxide (∿200mL) was refluxed with stirring for ∿10 min and allowed to stand for ∿4 min. The portion which settled out was isolated by decantation. This partially purified material was further purified by a succession of five like decantation steps. The resulting solid was recovered by filtration, washed with water and acetone, and dried (1.8g). The product, a blue powder in which was interspersed small amount of a dark powder, gave the expected powder X-ray diffraction lines[13,26] and three impurity lines.

The use of water buffered to a pH of 4 with potassium acid phthalate in the purification procedure led to a material grossly contaminated with decomposition products.

Modified Sintering Method. A mixture of CuO(1.27g), Na_2CO_3(0.848g), K_2CO_3(1.106g), SiO_2(3.85g), and $Na_2B_4O_7 \cdot 10H_2O$(0.707g) (a 2:1:1:8 mole-ratio mixture with 10% by weight of borax) was prepared. This was placed in a platinum crucible and heated to 675°C over ∿1h, held at this temperature for 1d, heated to 725°C over ∿1h, held at this temperature for 1d, heated to 760°C over ∿1h, and held at this temperature for 5d. The product, a hard, porous, blue solid with a shiny surface and black particles dispersed throughout (6.67g) was carefully broken out of the crucible (5.02g).

This solid was crushed to a powder that was virtually all <100 mesh. The few particles >100 mesh were rejected. A portion (2.00g) of the rest was purified using a decantation process like that described above (12 cycles). The product, a blue powder in which was interspersed a small amount of a dark powder, gave the expected powder X-ray diffraction lines and one low intensity impurity line (0.92g).

Because of the excess of sodium in the reaction mixture, this product could have contained $Na_2CuSi_4O_{10}$. However, the X-ray data did not give evidence for its presence.[15,29,32]

Devitrification Method. A 2:1:1:8 mole-ratio mixture of CuO, Na_2CO_3, K_2CO_3, and SiO_2 was heated in a platinum crucible to ∿1200°C. Part of the resulting glass was poured on a steel marver and flattened into a disc (1.31g). This was placed on a bed of $NaKCuSi_4O_{10}$ (6mg, <100 mesh) which was supported by a fused silica plate, and heated at 765°C for 12d. The product, a disc approximately the size of the original disc, was gently

pried from the silica plate (1.33g). It was composed mainly of a mass of
blue needle-like crystals oriented approximately perpendicularly to its
surfaces. Along with these were a small amount of a gray material, a small
silica shard, much of the powdered $NaKCuSi_4O_{10}$, and some blue glass. The
gray material was present as a thin layer on the top and sides of the disc
while the blue glass was present between the crystals. A powder of a portion
of the disc gave the expected diffraction lines and two impurity lines.

As is to be expected, the time required for substantial devitrification
of the glass employed under the general conditions used is variable. In an
experiment which was similar to that described except for the use of a thicker
disc of glass, 14d was insufficient but 28d was sufficient.

Instrumentation. The X-ray data were collected with a General Electric
XRD-5 spectrometer using cobalt radiation.

Discussion

Synthetic Work. The two sintering routes described for the synthesis
of litidionite are parallel to the two routes reported by Pabst for making
the chemically and structurally related silicate cuprorivaite (Egyptian
blue), $CaCuSi_4O_{10}$.[33,34] The devitrification route is probably parallel to
the route by which natural litidionite is formed since natural litidionite
occurs in association with a blue glass.[35]

Both the non-borax sintering route and the devitrification route
provide satisfactory methods for making the compound. The borax sintering
route is less satisfactory because it is experimentally more cumbersome
and may give a product which is less pure.

Structural Considerations. As already indicated fenaksite, agrellite, $Na_2CuSi_4O_{10}$, narsarsukite, miserite, and probably canasite contain, like lititionite, tube silicate ions.[13-19] The first three contain ions that are the same as that in litidionite while the fourth contains a different type of ion, Figure 2. Still another is found in miserite, Figure 3, and probably also in canasite.

Each of these three types of ions is structurally related to other silicate ions. Thus, as pointed out earlier,[36] the ion in narsarsukite is related to a well-known sheet ion found in, for example, kaolinite, $Al_2Si_2O_5(OH)_4$.[37]
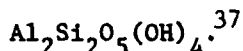
The basic relationship between these two ions is the same as that between their parent latticeworks. This relationship arises as is evident, Figure 4, because the pattern of the latticework tube taken circumferentially from a lengthwise line on its surface is the same as that in a strip of the latticework sheet.[38,39]

Similarly but not quite so directly, the ion in litidionite is related to a less common ion found in such silicates as apophyllite, $KCa_4Si_8O_{20}F \cdot 8H_2O$,[40] and cuprorivaite.[33] Here, again making reference to the parent latticeworks, the arrangement of the latticework tube is like that of a strip of the latticework sheet except that all the pendent units project from one surface, Figure 5. In the same manner the parent latticework of the ion in miserite is related to that of the ion in dalyite, $(K, Na)_2ZrSi_6O_{15}$,[41] Figure 6.[42]

All three of these latticework tubes are similar in that each is achiral and has a shortest circumferential circuit in which the repeat pattern occurs twice. However, in the first tube the shortest circuit does not incorporate a sequence of in-line links (i.e., links whose counterparts in

the corresponding strip are in a straight line). In the second and third tubes, in contrast, the shortest circuits do incorporate unbroken in-line sequences of links. Similarly, in the first tube no links in the circuit are parallel to a plane perpendicular to the tube axis while in the second and third tubes links in the circuits are parallel to planes perpendicular to the tube axes.

Additional latticework tubes associated with the kaolinite, apophyllite, and dalyite latticeworks are shown in Figure 7-9 (a variant of the third tube is associated with the dalyite latticework when arranged so as to outline squares and regular octagons). Each of these particular latticework tubes, like the first three latticework tubes, is achiral. Further, like the second and third of these tubes, each has a shortest circuit which contains two repeat patterns, incorporates an unbroken in-line sequence of links, and includes links that are parallel to a plane perpendicular to the tube axis.

Two latticework tubes associated with the latticework sheet corresponding to the ion in yet another sheet silicate, manganpyrosmalite, $(Mn,Fe)_8Si_6O_{15}(OH,Cl)_{10}$,[43] are shown in Figures 10 and 11.[44] These tubes too are achiral and have shortest circuits of the same nature as those in all but the first tube.

Many additional simple latticework tubes are also associated with the kaolinite, apophyllite, dalyite, and manganpyrosmalite latticework sheets. An example is the tube which is like the larger of the two tubes associated with the manganpyrosmalite sheet already discussed except for having a shortest circuit with one repeat, Figure 12. Another is the tube which is like the litidionite latticework tube except for having a shortest circuit with three repeats.

Not surprisingly many of these latticework tubes are chiral. A tube of this type associated with the apophyllite latticework sheet is shown in Figure 13. This tube, as is seen, has a shortest circuit which contains one repeat pattern, does not incorporate an unbroken in-line sequence of links, and does not include links parallel to a plane perpendicular to the tube axis.[45]

Still more latticework tubes similar to those already discussed exist. These are associated with additional latticework sheets.[47] Such a tube is shown in Figure 14.

Since there are so many closely related latticework tubes a simple systematic method for describing them is needed. This need can be met by utilizing descriptors containing the following elements: a c if the tube is chiral, a number giving the number of links in the shortest circuit, a subscript number giving the number of repeats in the circuit, and one or more numbers giving the number or numbers of links in the shortest circuit or circuits in the surface of the tube. Thus using this system the litidionite tube is the 6_2:4,8 tube.

In connection with the latticework tubes discussed, it is interesting to note that (using the system just outlined) the 8_2:4,8 tube, Figure 8, and the 10_1:4,6,12 tube, Figure 12, are isomers. It is also interesting to note that half the latticework strip associated with the 12_2:4,6,12 tube, Figure 10, has a drum-ladder counterpart, Figure 15. Obviously this is just one of a family of such latticeworks. So far no silicate based on a latticework of this type nor of the analogous chain-cage type is known.

As might be expected the known and potential silicate tubes have significant relationships with not just silicate sheets but also with other types

of silicate structures as well. One of these is the linear or chain-
band type.

Among the silicates that contain chains or bands with which the eight
known and potential silicate tubes discussed first have significant relation-
ships are: diopside, $MgCaSi_2O_6$,[48] howieite, $Na(Fe^{2+},Mg,Fe^{3+},Al)_{12}(Si_6O_{17})_2-$
$(O,OH)_{10}$,[49] aenigmatite, $Na_2Fe_5TiSi_6O_{20}$,[50] astrophyllite, $(K,Na)_3(Fe,Mn)_7-$
$Ti_2Si_8(O,OH)_{31}$,[51] tremolite, $Mg_5Ca_2Si_8O_{22}(OH,F)_2$,[52] jimthompsonite,
$(Mg,Fe)_5Si_6O_{16}(OH)_2$,[53] synthetic $Ba_5Si_8O_{21}$,[54] synthetic $Ba_6Si_{10}O_{26}$,[54]
vlasovite, $Na_2ZrSi_4O_{11}$,[55] xonotlite, $Ca_6Si_6O_{17}(OH)_2$,[56] tinaksite,
$K_2NaCa_2TiSi_7O_{19}(OH)$,[57] and nordite, $Na_2(Na,Mn)(Ca,Sr)RE(Zn,Mg,Fe,Mn)Si_6O_{17}$.[58]
The nature of some of these relationships is indicated in Figures 16 and 17.
Again the relationships are complicated in some cases, because of the posi-
tioning of the pendent oxygens.[59,60,62]

As is obvious, the known silicate tubes and the potential small to
moderate sized silicate tubes have (assuming reasonable bond parameters for
the latter) diameters covering a wide range. The lower end of this range
is $\sim 4\text{Å}$, Figures 1-3.[63]

Using past experience in similar situations as a guide, it appears
highly likely that silicate tubes of the narsarsukite, litidionite, and
miserite types will be found in silicates other than those in which they
are now known. Since the litidionite tube has been found in several sili-
cates, and since the relationships between it and several linear silicates
are strong, it is particularly likely that this tube will be found in other
silicates.

It also appears likely that new types of silicate tubes will be found
soon. Among the most likely to be found are those having the $8_2:6$, $8_2:4,8$,
and $6_2:4,6,8$ latticework tubes as parents since these latticework tubes

are like those which are parents of the litidionite and miserite tubes. The probability of finding the silicate tube whose parent is the 8_2:6 tube is further enhanced because of the close relationships that exist between it and known silicate bands.

As is evident latticework tubes of the types described cannot simultaneously have continuous single-link members running lengthwise and circumferentially. Tubes of this type are, however, found among those having four, five, and six members radiating from a junction, Figure 18.

Finally, it is probable that in some cases organic tubes having carbon or carbon-heteratom frameworks like those discussed can be made. Thus, since norpinane can be made,[64] it seems likely that tricyclo[3.1.1.^{2,4}]octane can be made and, hence, that narsarsukite-type and perhaps litidionite-type tubes can be made, Figure 19.[65] Such polymeric systems should have very interesting properties.

Acknowledgment

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38. For clarity the orientations of the tubes in Figures 2 and 4 are matched.

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44. As examination shows, the latticework tubes in Figures 10 and 4 and Figures 11 and 7 are close structural analogues.

45. The kaolinite, apophyllite, dalyite, and manganpyrosmalite parent latticework sheets are, as is apparent, based on three-connected networks. It is of interest to note that the first of these latticeworks is based on the only regular three-connected network and that the second and fourth are based on two of the three semiregular three-connected networks.[46] It is also of interest that the dalyite parent latticework can be derived formally from the kaolinite parent latticework by appropriate insertion of sets of links arranged in U's and the apophyllite parent latticework similarly can be derived from the dalyite parent latticework.

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47. These latticework sheets are also based, as they must be, on three-connected networks.

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60. As is clear, a close formal relationship exists between the chain in diopside and the bands in tremolite, jimthompsonite, and the synthetic barium silicates. It is thus interesting to note that the tremolite-type band in nephrite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$, is occasionally replaced by a triple-strand band.[61]

61. Hutchison, J. L.; Jefferson, D. A.; Mallison, L. G.; Thomas, J. M. Mater. Res. Bull. 1976, 11, 1557.

62. A real relationship may exist between the band in howieite, and its counter-part sheet since it has been suggested that the band is formed from the sheet by a shearing process.[49]

63. It should not be assumed, of course, that sizable channels or even any channels will exist in silicates having moderate sized tubes since the tubes may contain ions (as does the tube in miserite) or may not be fully extended (or both).

64. Musso, H.; Nauman, K. Angew. Chem. Int. Ed. Engl. 1966, 5, 127; Angew. Chem. 1966, 78, 116.

65. The litidionite-type tube having a carbon framework would be strained to an appreciable extent.

Figures

Figure 1. An ORTEP drawing of the tube ion in litidionite made with data gathered by Martin Pozas, Rossi, and Tazzoli.[13] The junctions indicate silicon atoms and the open circles oxygen atoms. The O_1-O_2 distance is 4.85Å.

Figure 2. An ORTEP drawing of the tube ion in narsarsukite based on data gathered by Peacor and Buerger.[36] The O_1-O_2 distance is 4.32Å.

Figure 3. An ORTEP drawing of the tube ion in miserite made with data gathered by Scott.[18] The O_1-O_2 distance is 7.53Å.

Figure 4. The parent latticework of the narsarsukite tube, this latticework opened along a lengthwise line and flattened, and the parent lattice-work of the kaolinite sheet with a strip emphasized that is the same as the opened and flattened tube latticework. The filled circles represent pendent units pointing outwards in the case of the tube and upwards in the case of the flat latticeworks. Like junctions have like numbers.

Figure 5. The parent latticework of the litidionite tube, this latticework opened, and the parent latticework of the apophyllite sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units. The filled circles represent pendent units pointing outwards or upwards and the open circles pendent units pointing downwards.

Figure 6. The parent latticework of the miserite tube, this latticework opened, and the parent latticework of the dalyite sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

Figure 7. A second latticework tube related to the parent latticework of
          the kaolinite sheet, this latticework opened, and the kaolinite
          latticework sheet with a strip emphasized that is the same as
          the opened-tube latticework.

Figure 8. A second latticework tube related to the parent latticework of
          the apophyllite sheet, this latticework opened, and the apophyllite
          latticework sheet with a strip emphasized that is the same as the
          opened-tube latticework except for the arrangement of the pendent
          units.

Figure 9. A second latticework tube related to the parent latticework of the
          dalyite sheet, this latticework opened, and the dalyite latticework
          sheet with a strip emphasized that is the same as the opened-tube
          latticework except for the arrangement of the pendent units.

Figure 10. A latticework tube related to the parent latticework of the mangan-
           pyrosmalite sheet, this latticework opened, and the manganpyrosmalite
           latticework sheet with a strip emphasized that is the same as the
           opened-tube latticework except for the arrangement of the pendent
           units.

Figure 11. A second latticework tube related to the parent latticework of the
           manganpyrosmalite sheet, this latticework opened, and the mangan-
           pyrosmalite latticework sheet with a strip emphasized that is the
           same as the opened-tube latticework except for the arrangement of
           the pendent units.

Figure 12. A latticework tube related to the larger of the two latticework
           tubes associated with the manganpyrosmalite latticework sheet.

Figure 13. A chiral latticework tube related to the apophyllite latticework
sheet. A part of a series of links following a generally helical
path is emphasized.

Figure 14. A latticework tube related to a pentagon-octagon latticework, this
latticework opened, and the pentagon-octagon latticework with a
strip emphasized that is the same as the opened-tube latticework.

Figure 15. The latticework drum-ladder structure related to the 12_2:4,6,12-
latticework tube.

Figure 16. Relationships between known and potential silicate tubes and known
silicate linear structures. The frameworks are those of strips
corresponding to the tubes. Superimposed on these are the lattice-
works of the linear systems. These are altered, as necessary, by
minor or significant amounts. The latticework-framework pairs shown
are: (a) the diopside- and howieite-narsarsukite pairs, (b) the
diopside-, aenigmatite-, astrophyllite-, tremolite-, jimthompsonite-,
$Ba_5Si_8O_{21}$-, and $Ba_6Si_{10}O_{26}$-8_2:6 pairs, (c) the diopside-,vlasovite-,
xonotlite-, and tinaksite-litidionite pairs, and (d) the diopside-
and aenigmatite-8_2:4,8 pairs. In those cases where the latticeworks
are substantially unaltered the directions of the pendent units are
indicated: short lines, filled circles, and open circles represent-
ing respectively units pointing sideways, upwards, and downwards;
and triangle-short line combinations representing pairs of units
pointing at an angle. In the remaining cases only the presence of
the pendent units is indicated: square-short line combinations
representing groups of two or three units.

Figure 17.   Additional relationships between known and potential silicate tubes
and known silicate linear structures. The latticework-framework
pairs shown are: (a) the diopside-, and xonotlite-miserite pairs,
(b) the diopside, aenigmatite-, and howieite-6_2:4,6,8 pairs, (c)
the diopside and nordite-12_2:4,6,12 pairs, and (d) the diopside-
and vlasovite-20_2:4,6,12 pairs (for economy only half the
12_2:4,6,12 and 20_2:4,6,12 frameworks are shown).

Figure 18.   Tubes with single-link members running lengthwise and circumferen-
tially: (a) a tube with four units at each junction, (b) a tube with
five units at each junction, and (c) a tube with six units at each
junction.

Figure 19.   The structures of: (a) norpinane, (b) tricyclo[3.1.1.1^{2,4}]octane,
(c) the hypothetical narsarsukite-type polymer, and (d) the
hypothetical litidionite-type polymer.
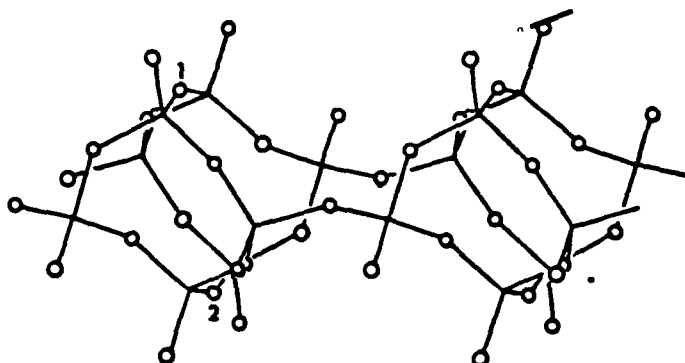
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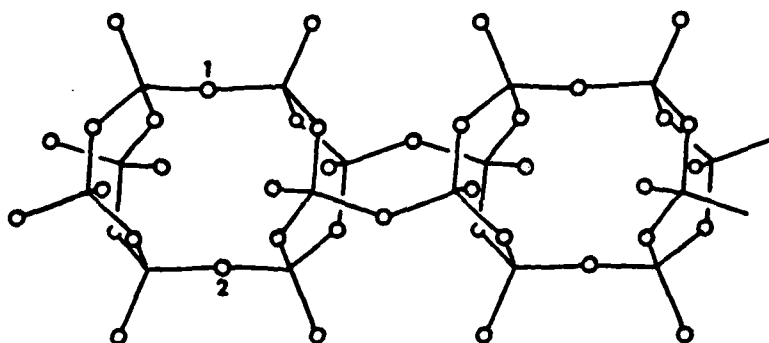
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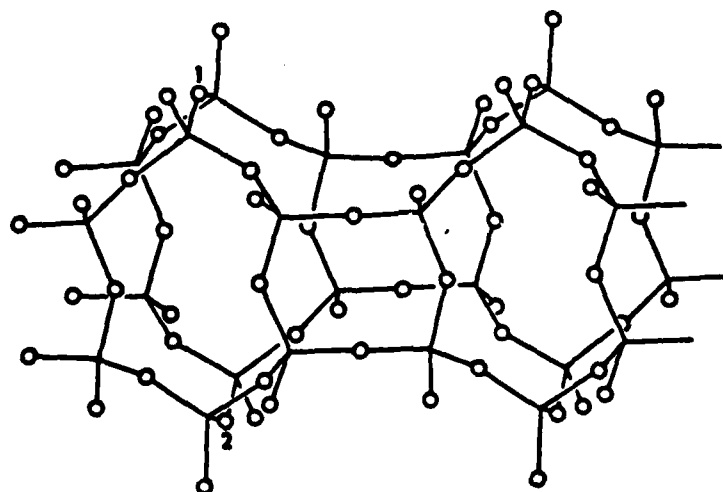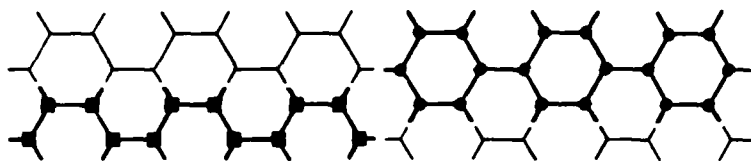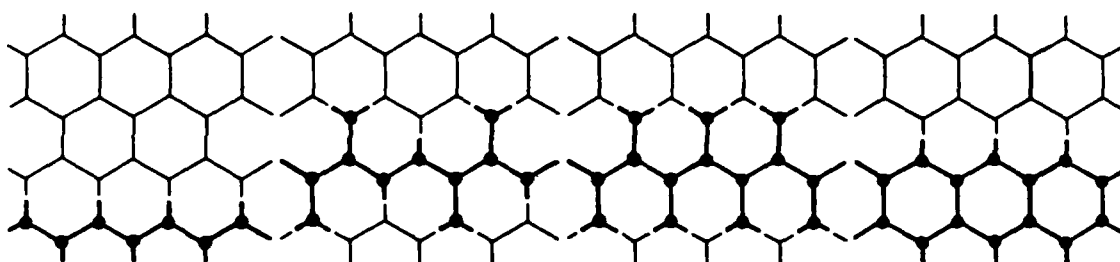

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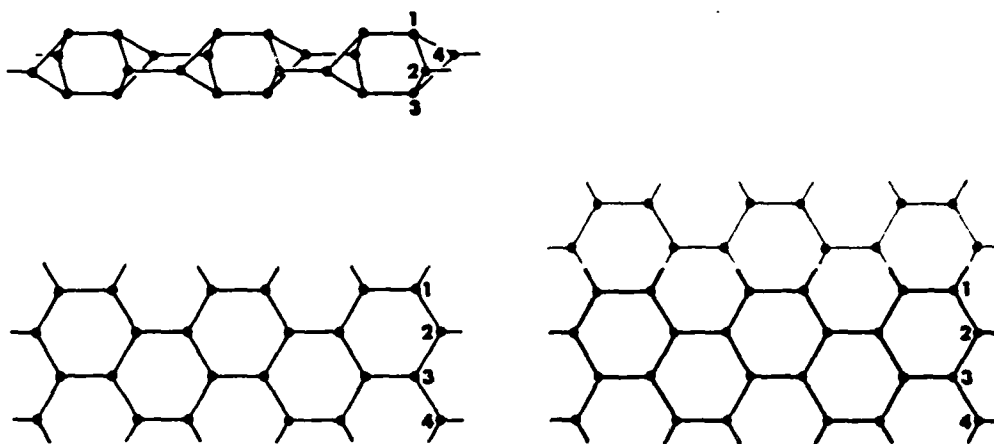
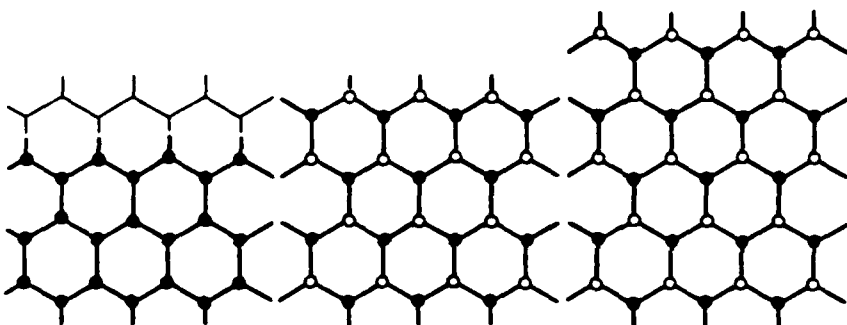Fig 4
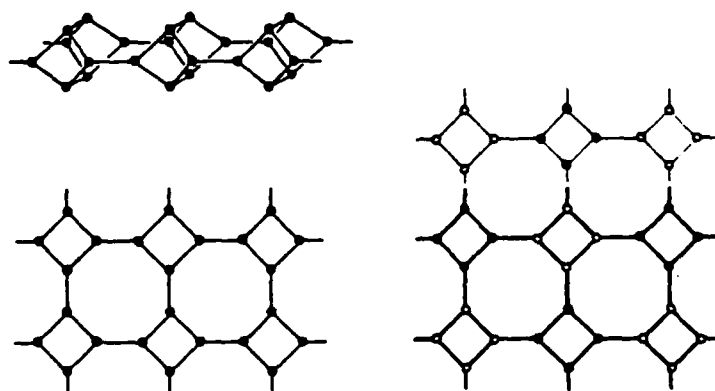
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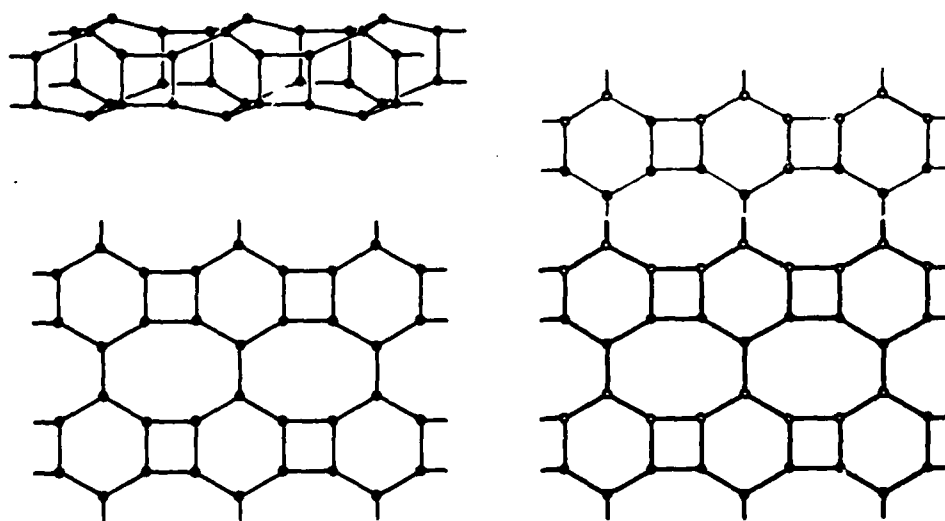
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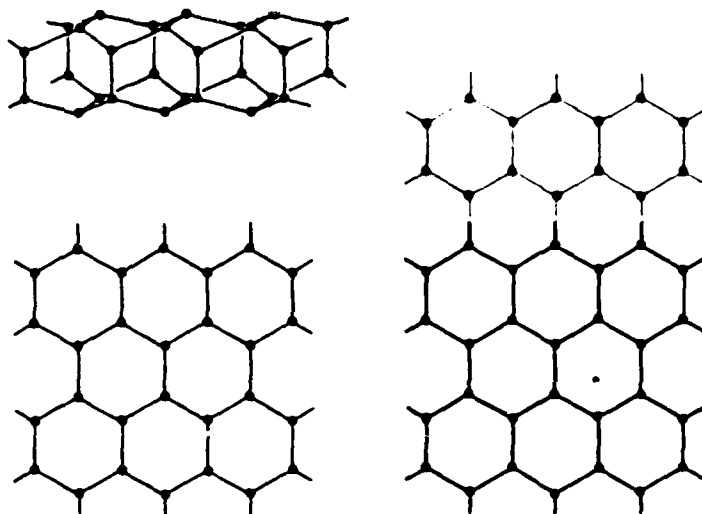
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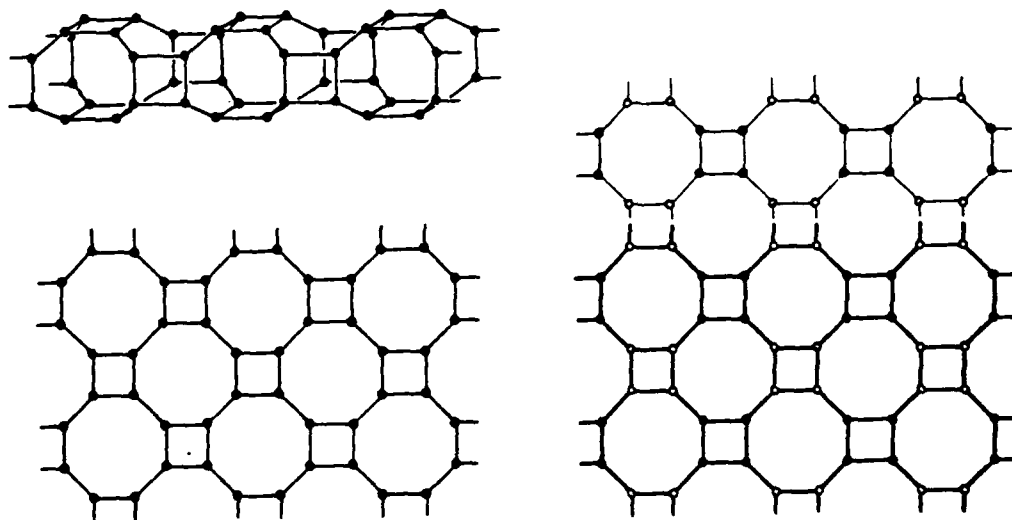
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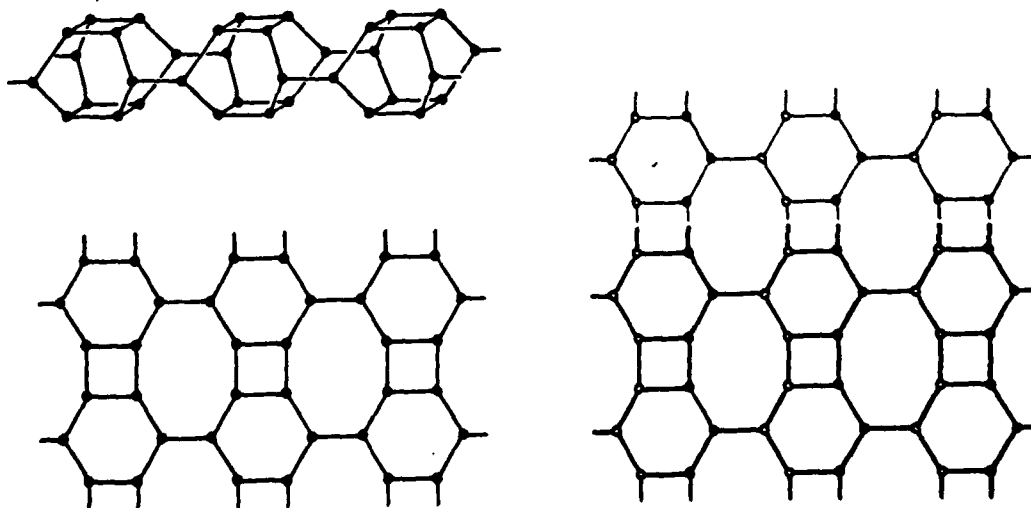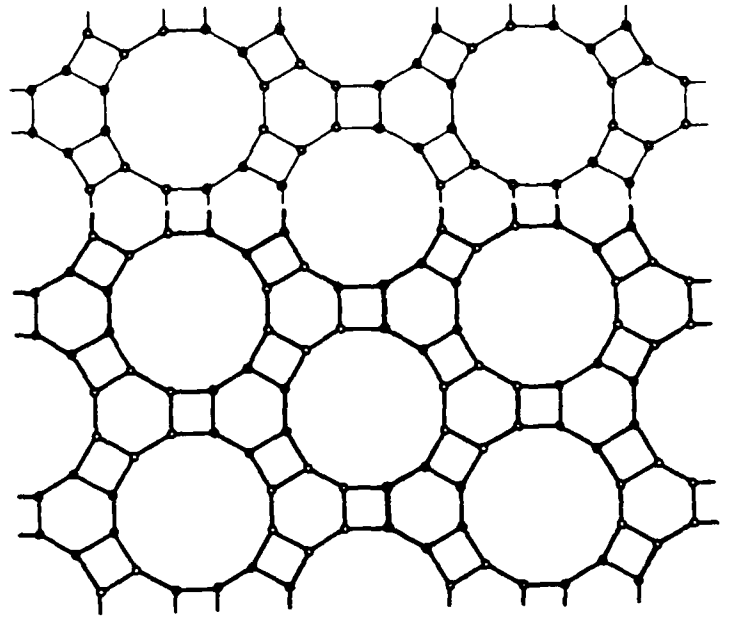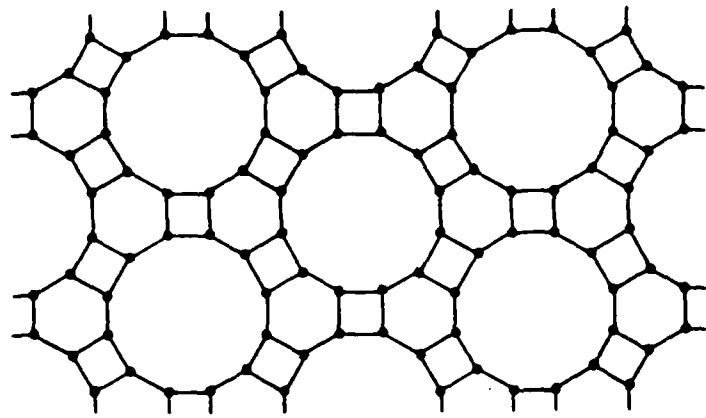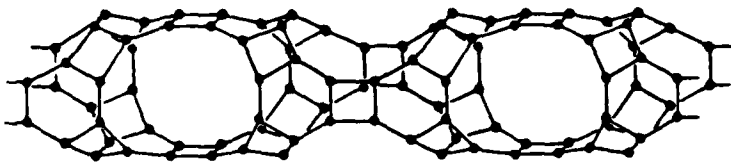
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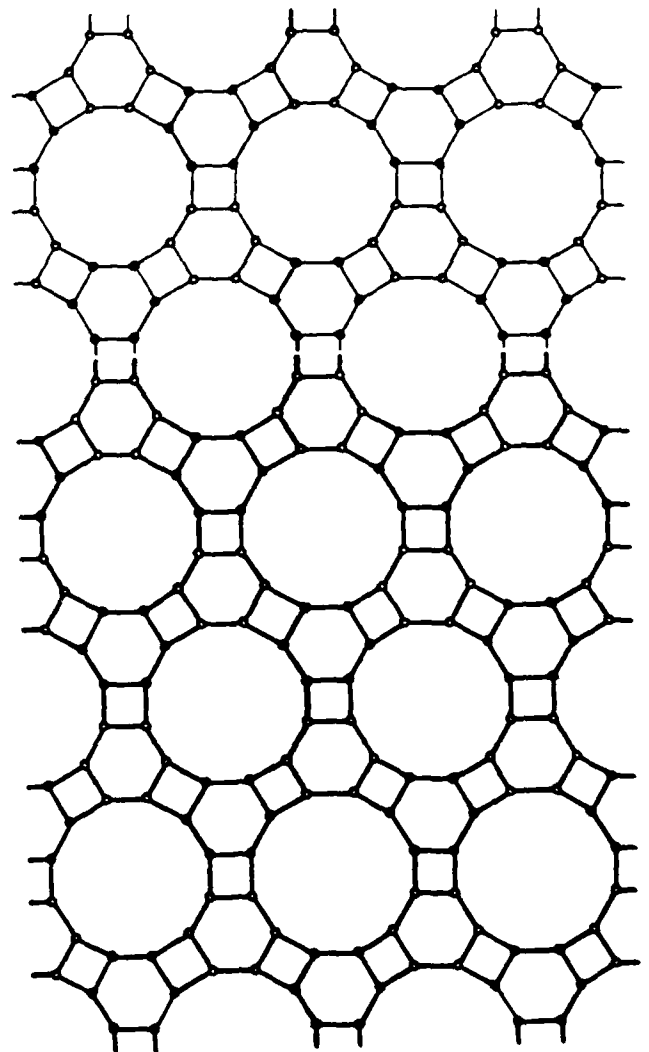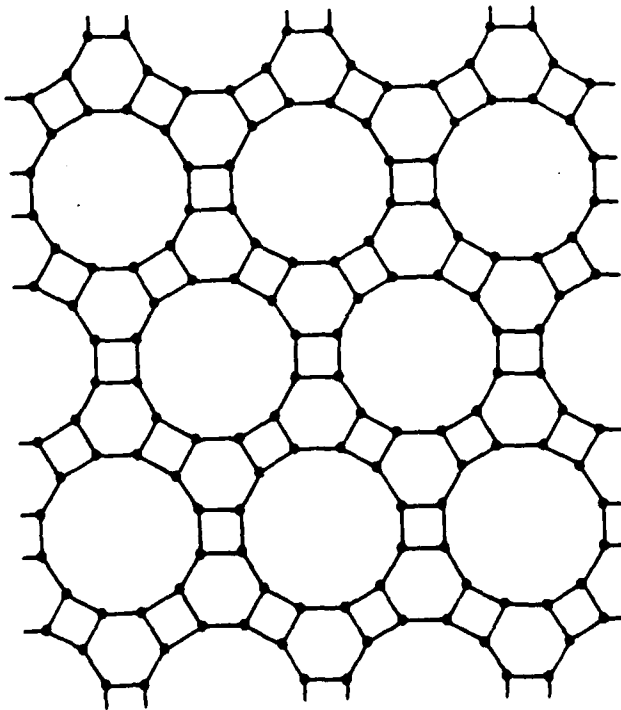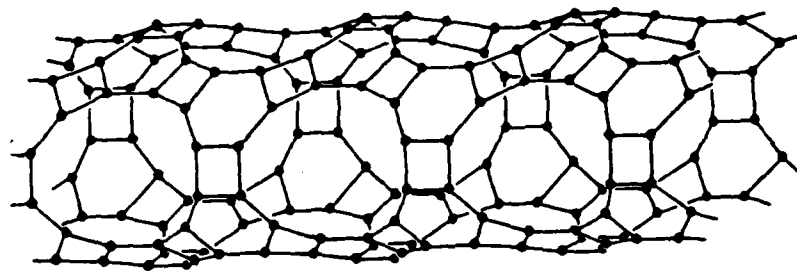
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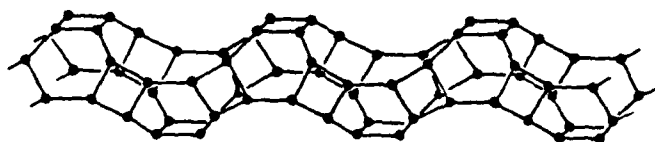
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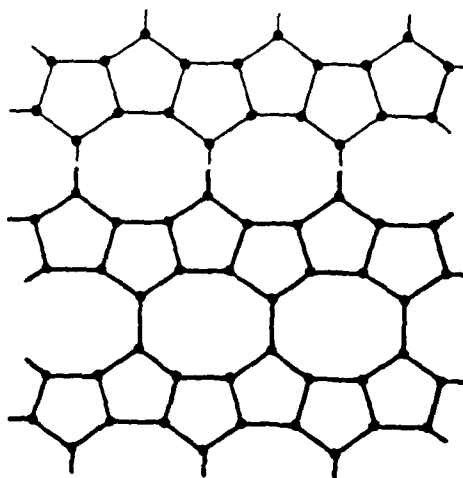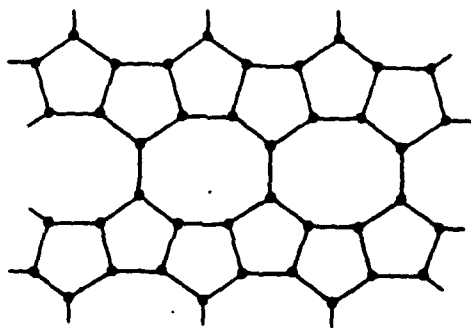
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Fig 15

a

b

c

d

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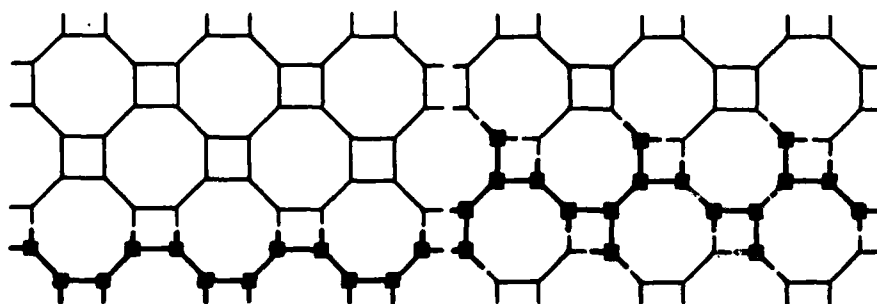
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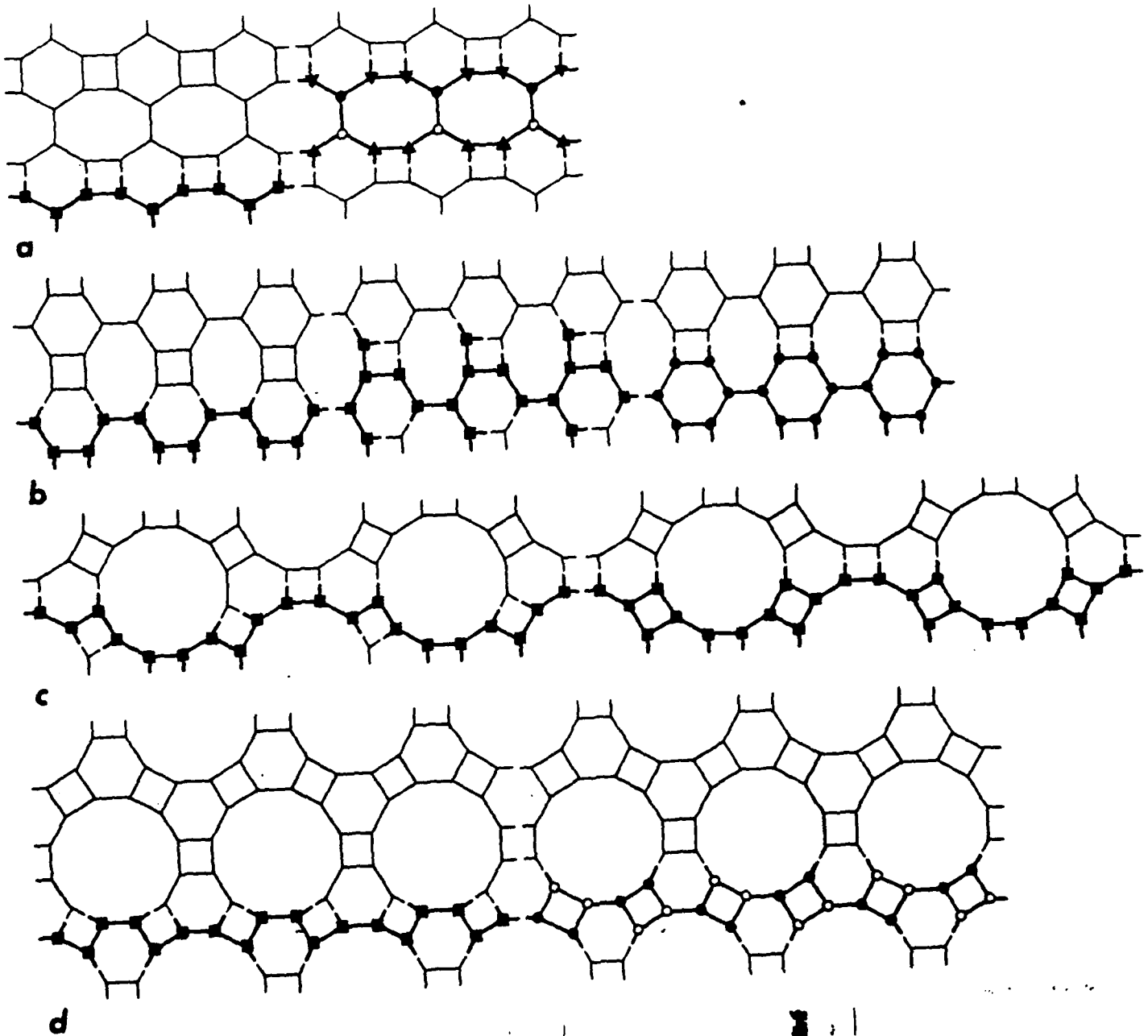
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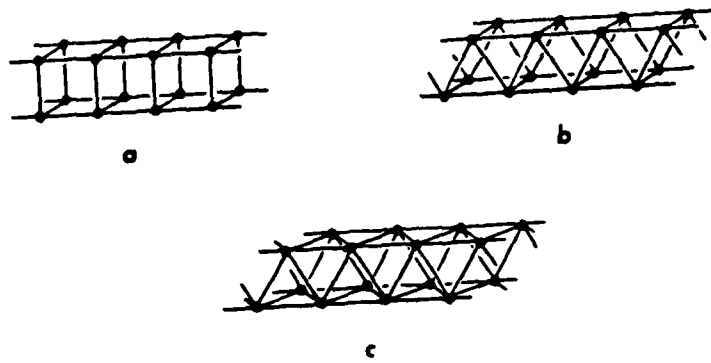
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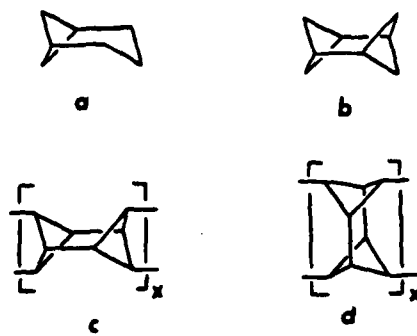
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